Chemical Engineering Journal 254 (2014) 302–312

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Synergistic adsorption and reduction of hexavalent chromium using highly uniform polyaniline–magnetic mesoporous silica composite

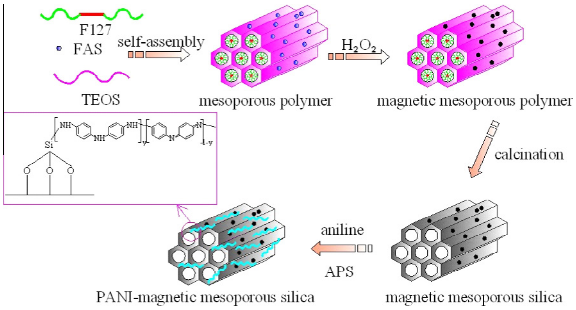
Lin Tang [a,b,*], Yan Fang [a,b], Ya Pang [c], Guangming Zeng [a,b,*], Jiajia Wang [a,b], Yaoyu Zhou [a,b], Yaocheng Deng [a,b], Guide Yang [a,b], Ye Cai [a,b], Jun Chen [a,b]

[a] *College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China*
[b] *Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, Hunan, PR China*
[c] *Department of Biological Engineering and Environmental Science, Changsha College, Changsha 410003, PR China*

HIGHLIGHTS

- Highly uniform magnetic mesoporous silica composite with polyaniline grafted was applied to highly efficient Cr(VI) removal.
- The mechanism of adsorption and synergistic reduction has been ascertained.
- High capacity for the removal of Cr(VI) was observed.
- The adsorbent showed excellent reproducibility and selective adsorption ability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 26 May 2014
Accepted 27 May 2014
Available online 4 June 2014

Keywords:
Polyaniline
Magnetic mesoporous silica
Hexavalent chromium
Adsorption
Reduction

ABSTRACT

In this study, a novelly synthesized magnetic mesoporous silica composite with high uniformity and polyaniline (PANI) grafted was successfully applied to highly efficient Cr(VI) removal. With the assistance of high adsorption capacity of protonated PANI and the magnetic mesoporous composite at low pH, Cr(VI) was adsorbed and then reduced to less toxic Cr(III) by PANI. The resultant adsorbent was characterized by TEM and FTIR, nitrogen adsorption–desorption measurements were carried out, and the zeta potentials of the prepared adsorbent were also measured at different pH. The adsorption and synergistic reduction route was particularly deduced by analyzing the existing forms of PANI and Cr by XPS. Pseudo-second-order model could well fit the data obtained from batch Cr(VI) removal experiments for the kinetic study, and Langmuir model well described the sorption isotherms with the maximum adsorption capacity of 193.85 mg/g. Competition from coexisting ions (K^+, Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-) was proved to be insignificant. Moreover, the exhausted adsorbent could be well regenerated and kept above 83% removal efficiency in the first three cycles, which demonstrated that it was cost-effective. The results suggested that this novel magnetic adsorbent may offer a simple adsorption and synergistic reduction treatment option to remove Cr(VI) contamination from industrial wastewater and natural water bodies.

1. Introduction

Hexavalent chromium (Cr(VI)) is a highly toxic pollutant, which is able to cause carcinogenesis, mutation to humans and animals, and has been designated as one of the top-priority toxic pollutants by the US Environmental Protection Agency [1–3]. Chromium (Cr)

---

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel./fax: +86 731 88822778.
E-mail addresses: tanglin@hnu.edu.cn (L. Tang), zgming@hnu.edu.cn (G. Zeng).

http://dx.doi.org/10.1016/j.cej.2014.05.119
1385-8947/

is generated by anthropogenic activities such as metal finishing, electroplating, leather tanning and chromate production, and etc. [4]. Therefore, developing effective methods to remove Cr(VI) from the environment is of great significance to human health and ecological system. Among treatment methods of aqueous Cr(VI), such as adsorption, coagulation, electrochemical precipitation, oxidation–reduction, reverse osmosis and ion exchange [4,5], adsorption is one of the most attractive and effective choices, because of its wide raw material sources, simple operation, easy recovery, high effectiveness, and etc. To date, many adsorbents have been applied for metal ions removal, such as chitosan [6], zeolites [7], clay minerals [8], organic resins [9], and even some industrial waste, like fly ash [10]. However, how to increase the removal efficiency and simplify the reuse and recovery process of the adsorbents still needs to be further studied.

Recently, magnetic mesoporous material [11,12] as adsorbent carrier has drawn increasing attention due to their chemical modifiable surface, magnetic property, large specific surface area and pore volume that exhibit advantages in terms of mass diffusion and transport. Besides, Yuan et al. found the synthetic mesoporous Fe/carbon composites were superparamagnetic and could be separated by applying an external magnetic field instead of centrifugation or filtration, leading to lower cost and easier operation [13]. A typical method to prepare magnetic mesoporous silica in literatures included two steps: preparing Fe_3O_4 nanoparticles, and then mixing them with a Si precursor and template, such as P123 or F127. But the magnetic distribution of the obtained materials was usually uneven because of the aggregation of Fe_3O_4 nanoparticles. In order to overcome this defect, in this work, an in situ synthesis route was proposed to prepare magnetic mesoporous silica.

Previous studies indicated surface modification of magnetic mesoporous materials by organic functional groups can highly improve their performance in metal ions removal [14]. The functional groups like carboxyl, hydroxyl, and thiol groups were responsible for heavy metals adsorption, due to their affinity for the metal ions to form complex [15]. Particularly, surface protonation of the materials under the acid condition and consequent electrostatic interaction with different oxyanionic forms of Cr(VI) were conducive to the Cr(VI) removal [1]. Therefore, selecting a suitable organic substance to modify the magnetic meosoporous composites is of great importance in developing highly efficient adsorbent toward Cr(VI) removal. Polyaniline (PANI), a well-known conducting polymer, has three idealized oxidation states, leucoemeraldine, emeraldine and pernigraniline, corresponding to reduced, doped and oxidized states, respectively [16]. It has been widely used in battery electrodes, sensors, electromagnetic shielding devices, and anticorrosion coatings [17]. Moreover, it has been subjected to studies as a reductant because of its excellent redox reversibility. The use of PANI for the reduction of very toxic Cr(VI) to less toxic Cr(III) has been reported [18,19]. In short, PANI can be utilized to remove Cr(VI) efficiently due to the existing of large quantities of amine groups and imine groups, which not only owns specific affinity sites for heavy metals, but also can reduce Cr(VI) to Cr(III) spontaneously.

In our study, a highly uniform magnetic mesoporous silica composite was in situ synthesized by mixing ferric iron precursor, F127 and TEOS, evenly, oxidizing Fe^{2+} to Fe_3O_4 by H_2O_2, and finally grafting with PANI to functionalize the composite. The resultant adsorbent was characterized by TEM, FTIR, and XPS, and nitrogen adsorption–desorption isotherms and zeta potential were also measured. Moreover, the influence of several operating parameters for adsorption of Cr(VI), such as contact time, pH, and initial concentration of Cr(VI), were investigated in batch mode. The adsorption and synergistic reduction route of Cr(VI) was particularly deduced. The kinetics data were fitted with different models, and the isotherm equilibrium data were fitted with Langmuir and Freundlich model. The competitive effect of common co-existing ions and the regeneration were also investigated.

2. Materials and methods

2.1. Materials

Pluronic®F-127 was purchased from Sigma (Sigma–Aldrich, USA). All other chemicals, including tetraethyl orthosilicate (TEOS), 2-2-diphenylcarbonic dihydrazide, $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (FAS), HCl, H_3PO_4, H_2SO_4, NaOH, H_2O_2, ethanol, potassium dichromate, and ammonium persulfate (APS) were of reagent grade and used as received without further purification. Aniline was distilled under vacuum prior to use. Chromium standard solutions (1000 μg/mL) were diluted to establish standard curve. Ultrapure water (18.25 MΩ/cm) was used throughout the whole experiments.

2.2. Preparation of magnetic mesoporous silica

The magnetic mesoporous silica was synthesized according to the procedure described in the literature [20] with some alterations. Briefly, 4 g F-127 was dissolved in 200 mL of 0.1 mol/L HCl solution, followed by adding 35.2 g ammonium ferrous sulfate and stirred until totally dissolved. Then 18.6 g TEOS was added into the mixture. After these operations, the molar ratio of Fe to Si is 1. The mixture was mechanically stirred in an ice bath for 8 h to obtain clear liquid. The obtained clear liquid was transferred into digestion tank and kept for 24 h at 100 °C. Then the resulting solid was collected by centrifugation, and then immersed in 300 mL of 0.1 mol/L NaOH in water bath at 60 °C, and 350 μL of 30% H_2O_2 was added into the liquid with mechanical stirring for 1 h, and then Fe_3O_4 was produced via oxidation of Fe^{2+}. The collected solid matter was washed repeatedly and dried under vacuum in oven at 100 °C. Magnetic mesoporous silica was obtained by temperature-programmed calcination at 550 °C for 6 h with a heating rate of 2 °C per hour. The calcination procedures were protected under nitrogen atmosphere.

2.3. Grafting of PANI to magnetic mesoporous silica composite

PANI–magnetic mesoporous silica composite was prepared by in situ polymerization of aniline [17,21]. Typically, 1.83 mL aniline monomer was dissolved in 50 mL of 1 mol/L hydrochloric acid solution and stirred for 1 h. 0.39 g magnetic mesporous silica was added into 100 mL ethanol, and the mixture was further mixed with the above solution. Then, 4.56 g APS was dissolved in 50 mL of 1 mol/L hydrochloric acid solution to prepare APS solution. The obtained oxidation liquid was added dropwise to the prepared solid–liquid mixtures to polymerize aniline. The reaction was kept in an ice bath and stirred slowly for 24 h. After the polymerization, the solid sample was washed with ethanol and ultrapure water in sequence until the supernatant was colorless. Finally, the material was dried in vacuum at 60 °C for 24 h. The schematic diagram is shown in Fig. 1.

2.4. Characterization of PANI–magnetic mesoporous silica composite

The characterization of PANI–magnetic mesoporous silica composite was conducted by transmission electron microscopy (JEOL-1230), FTIR spectrometer (WQF-410), Zetasizer Nano (ZEN3600, Malvern), Pore size Analyzer (QuadraSorb Station 3). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, UK) was used to characterize the surface chemistry of loaded chromium and nitrogen atom of the adsorbent before and after the treatment.